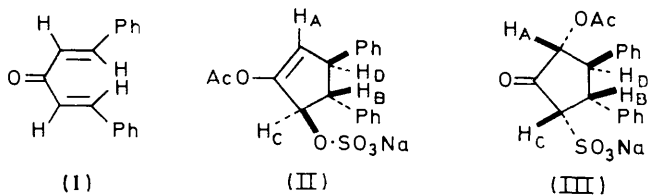


## Electrocyclic Reactions. Part V.<sup>1</sup> The Structure of the Product from *trans,trans*-Dibenzylideneacetone and Sulphuric Acid–Acetic Anhydride

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Carbon-13 n.m.r. spectrometry leads unequivocally to the assignment of sodium *c*-3-acetoxy-2-oxo-*t*-4,*c*-5-diphenylcyclopentane-*r*-1-sulphonate (III), and necessitates revision of the cyclopentenyl structure (II) originally suggested, as the product obtained from *trans,trans*-dibenzylideneacetone and conc. sulphuric acid–acetic anhydride.

In Part II,<sup>2</sup> we suggested that the product, C<sub>19</sub>H<sub>17</sub>NaO<sub>6</sub>S, obtained by Vorlander and Schroedter<sup>3</sup> from *trans,trans*-dibenzylideneacetone (I) by the action of conc. sulphuric acid and acetic anhydride at 25–30°, had the structure (II). This structure was mechanistically attractive, and was consistent with all the chemical and physical data except for the <sup>1</sup>H n.m.r. coupling constant  $J_{AD}$  12 Hz, which is too large for a torsion angle  $\theta_{AD}$  *ca.* 60°, and to which we drew attention.



We have therefore considered the alternative formula (III), which is also consistent with the u.v. and i.r. data, and also satisfies the size of the coupling constant  $J_{AD}$ ,

of the sodium salt (III) in 99.5% [<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide solution exhibited fourteen singlet signals at  $\delta$  20.2, 47.9, 50.8, 71.1, 80.4, 126.4, 127.2, 127.4, 128.0, 128.4, 138.1, 141.5, 169.1, and 201.7 (Figure 1) as compared with the fifteen singlet signals expected from the nineteen carbon atoms in the molecule; the missing singlet signal represents one of the six tertiary aromatic carbon atoms and is presumably coincident with the signal of one of the other five relevant tertiary aromatic carbon atoms.

A second <sup>13</sup>C n.m.r. spectrum was obtained by off-resonance single frequency heteronuclear decoupling, and showed (Figure 2) a single quartet for a methyl carbon atom, four doublets for methine carbon atoms, and three unchanged singlets for non-proton bearing carbon atoms. The unchanged off-scale singlet for the carbonyl carbon atom (C-2) is not reproduced in Figure 2. The tertiary aromatic carbon atoms appear as seven singlets and not as discernible doublets presumably on account of overlapping as a consequence of the small chemical shift differences.

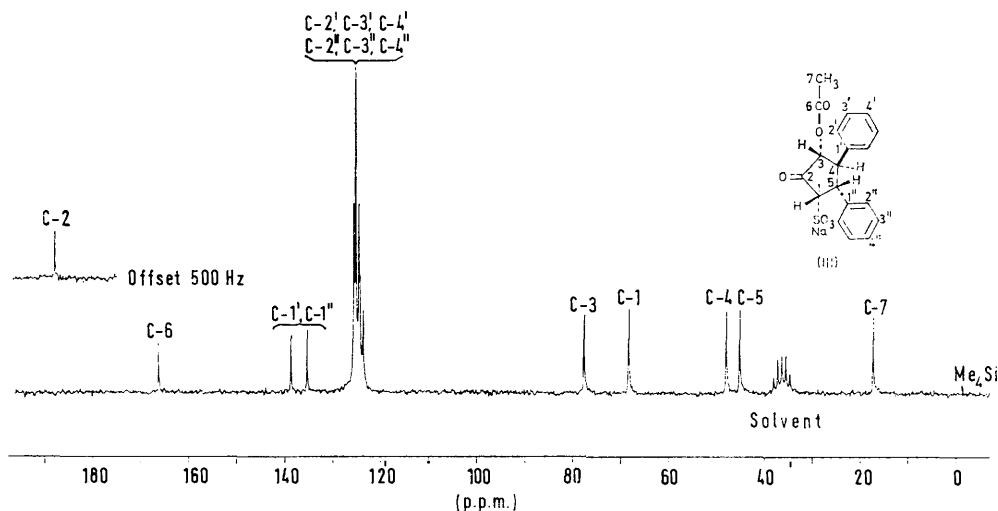


FIGURE 1 Compound (III): 25.18 MHz <sup>13</sup>C Fourier transformed, 2000 transients, proton-noise decoupled n.m.r. spectrum in (CD<sub>3</sub>)<sub>2</sub>SO

since  $\theta_{AD}$  is now *ca.* 120°, and accounts for  $J_{AO}$  in terms of the **W**-rule<sup>4a</sup> and for the chemical shift of the proton H<sub>C</sub> situated on carbon directly attached to sulphur.<sup>4b</sup>

The correctness of structure (III) is proved by the carbon-13 n.m.r. spectra. The initial <sup>13</sup>C n.m.r. spectrum

<sup>1</sup> Part IV, C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1973, 2197.

<sup>2</sup> C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I*, 1972, 2271.

The genesis of compound (III) appears to involve formation of the conjugate of *trans,trans*-dibenzylideneacetone, not with the acylium ion as previously suggested,<sup>2</sup> but with a proton to give the pentadienyl cation (A) which

<sup>3</sup> D. Vorlander and G. Schroedter, *Ber.*, 1903, **38**, 1490; cf. H. J. von Libig, *Annalen*, 1914, **405**, 188.

<sup>4</sup> L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 2nd edn., 1969, (a) p. 234; (b) p. 177.

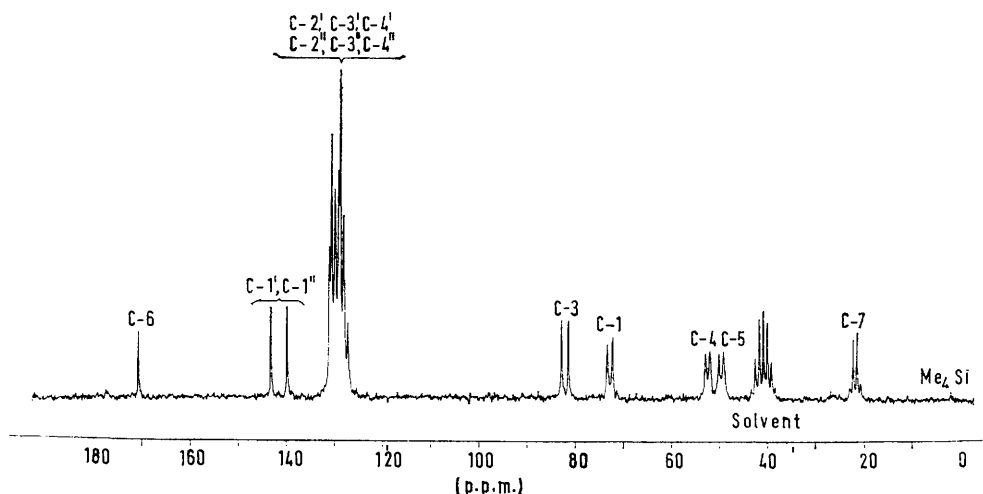
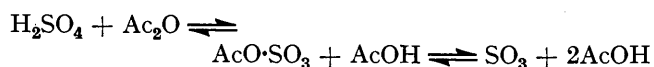
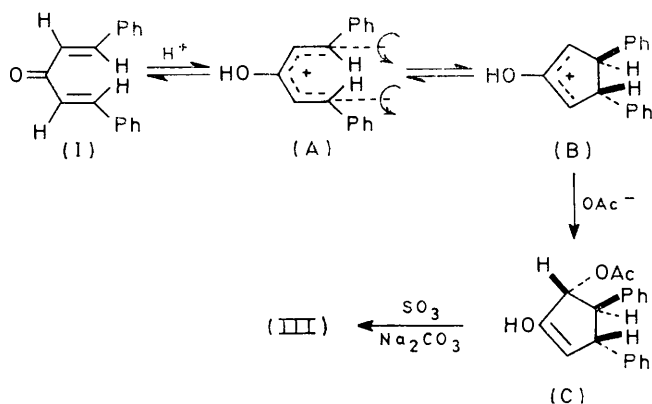


FIGURE 2 Compound (III): 25.18 MHz  $^{13}\text{C}$  Fourier transformed, 6140 transients, off-resonance decoupled spectrum (irradiation at 3.0 p.p.m. upfield from  $\text{Me}_2\text{Si}$ ) in  $(\text{CD}_3)_2\text{SO}$

undergoes a thermal conrotatory electrocyclic reaction to yield the cyclopentenyl cation (B). This, as the canonical form, co-ordinates with an acetate ion to give the enol (C), which undergoes sulphonation by sulphur trioxide,<sup>5</sup> by a mechanism analogous to that of acid catalysed bromination of ketones.<sup>6</sup>



The ready conversion of the compound (III) by warm aqueous sodium carbonate into Vorlander's ketol (VIII), sodium sulphite, and sodium acetate is now readily



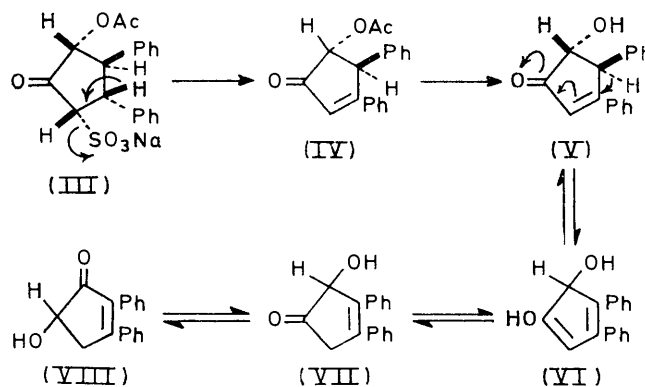
explicable in terms of a *trans*- $\beta$ -elimination process [(III)  $\rightarrow$  (IV)], with prior, concomitant, or subsequent ester hydrolysis of the acetate group [(IV)  $\rightarrow$  (V)], followed by vinylogous enolisation [(V)  $\rightleftharpoons$  (VI)] and prototropy [(VI)  $\rightleftharpoons$  (VII)  $\rightleftharpoons$  (VIII)].

<sup>5</sup> E. E. Gilbert, *Chem. Rev.*, 1962, **62**, 555, 558.

<sup>6</sup> E. E. Gilbert, 'Sulphonation and Related Reactions,' Interscience, New York, 1965, pp. 37-41.

#### EXPERIMENTAL

*Sodium c-3-Acetoxy-2-oxo-t-4,c-5-diphenylcyclopentane-1-sulphonate* (III).—The sodium salt trihydrate<sup>3</sup> was prepared from the potassium salt monohydrate<sup>3</sup> as described



previously,<sup>2</sup> and recrystallised from 50% aqueous methanol, m.p. *ca.* 240° (decomp.). Its  $^{13}\text{C}$  n.m.r. spectra were obtained on a Varian XL-100-15 spectrometer, operating in the Fourier transform mode at 25.18 MHz for carbon-13 with (a) proton noise decoupling at 100 MHz (Figure 1), (b) off-resonance single frequency decoupling at 300 Hz upfield from the internal reference (tetramethylsilane) (Figure 2); the solvent was  $[\text{2H}_6]$ dimethyl sulphoxide. Data were accumulated in a Varian 620 computer using 6000 Hz sweep width in 8192 points; the pulse width was 40  $\mu\text{s}$ , and the data acquisition time was 0.666 s. The number of pulses (transients) are recorded in Figures 1 and 2.

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